

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-080594

(43)Date of publication of application : 26.03.1999

(51)Int.Cl.

C09D 4/02
C08F230/02
C08F230/08
C08F290/06
C09D 5/00
C09D143/00
G03F 1/14

(21)Application number : 09-249362

(71)Applicant : TOAGOSEI CO LTD

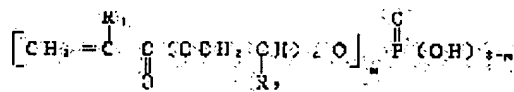
(22)Date of filing : 29.08.1997

(72)Inventor : FUJIWARA MASAHIRO
OFUSA KAZUKI
TAGUCHI HIROKANE

(54) RESIN COMPOSITION FOR COATING AND PHOTOMASK COATED THEREWITH

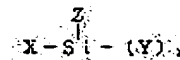
(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject composition capable of providing a coating film excellent in antistatic ability, hardness, adhesion, UV transmissivity and water resistance and useful as a photomask or the like by compounding a polymerizable acid phosphoric ester with a specific silane compound in a specified proportion.



I

SOLUTION: This coating composition is obtained by compounding (A) a polymerizable acid phosphoric ester represented by formula I [R₁ is H or methyl; R₂ is H, methyl or a halogenated methyl; (m) is 1 or 2; (n) is an integer of 1-8] or the like (e.g. 2-methacryloyloxyethyl acid phosphate) with (B) a silane compound represented by formula II (X is an organic group having an ethylenically unsaturated double bond; Y is an alkoxy; Z is an alkoxy or an alkyl) (e.g. 3-methacryloxypropyltrimethoxysilane) and (C) an organic compound having ≥2 polymerizable unsaturated double bonds in one molecule (e.g. polyethylene glycol diacrylate). The amounts of the compounded components are 21-40 wt.% component A, 3-30 wt.% component B and 30-76 wt.% component C.



II

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the
examiner's decision of rejection or application
converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of
rejection]

[Date of requesting appeal against examiner's
decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

* NOTICES *

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the photo mask with which it has sufficient antistatic ability, a high degree of hardness, good adhesion, and high ultraviolet-rays permeability in more detail, and has this protective coating in the resin constituent for covering which can offer a protective coating also with a good water resisting property, and a list about the photo mask which makes a protective coating the hardened material of the resin constituent for covering, and this constituent.

[0002]

[Description of the Prior Art] In the production process of the shadow mask of a printed wired board or the Braun tube, the exposure process which irradiates ultraviolet rays ("UV" is called below.) is in through and a photopolymer about the photo mask of glass or the product made from polyethylene terephthalate. At an exposure process, since only the part by which UV was irradiated becomes insoluble to a developer, or meltable alternatively, the resin pattern of the target configuration can be reproduced. Here, since the width of face and spacing of a line are as precise as dozens - 100 micrometers of numbers, on a photopolymer, it will become a shadow, and will appear, and the target image will not be obtained, but the image of a photo mask will serve as a defective, if a blemish is attached to the image of a photo mask. Then, a photo mask covers a front face with a protective coating with abrasion-proof nature, and prevents attaching a blemish to an image in many cases. This protective coating has the high permeability of UV, and needs to be able to form in smooth and thin thickness moreover. In a protective coating with low UV permeability, since UV is absorbed by this protective coating, before reaching a photopolymer, reinforcement will need to fall, and it will be necessary to take the long exposure time, and the fall of productivity will be caused.

[0003] Although what has a high degree of hardness is desirable because of abrasion-proof nature as for a protective coating, if dust adheres on a photo mask, since it will become a shadow and will appear on a photopolymer too, the target image is not obtained. For this reason, the protective coating is expected to have antistatic ability in order to prevent the adhesion of dust other than a high degree of hardness. As a means to give antistatic ability to a protective coating, the technique of carrying out addition kneading **** of the surfactant conventionally, the technique of applying the partial hydrolysate of a silicate compound, and the technique of adding a conductive filler are known. However, addition of a surface active agent has the fault that the surface active agent of the front face which carried out bleed out reduces dedropping and adhesion with a base material by rinsing etc. The process applied and hardened again is required for spreading of a silicon system compound on the protective coating formed once. Addition of a conductive filler is insufficiently transparent upwards, and expensive.

[0004] The technique of giving antistatic ability to a protective coating is reported by on the other hand copolymerizing a monomer with antistatic ability. For example, in JP,56-139516,A, polyalkylene glycol mono-methacrylate is used as a monomer with antistatic ability. Since copolymerization is performed, although solved, the effectiveness of electrification prevention needs a lot of low addition, and, as for the problem of omission by rinsing, polyalkylene glycol mono-methacrylate causes the fall of other physical properties.

[0005] On the other hand, the example using the high polymerization nature alkyl acid phosphate of the antistatic effectiveness is reported. Although sufficient antistatic ability was obtained by addition of a constant rate, polymerization nature alkyl acid phosphate had the problem that the water resisting property of a protective coating got worse, when it added so much, as indicated by JP,4-67731,A. As indicated by JP,61-73709,A, JP,61-78807,A, **** No. 207358 [62 to], JP,64-33169,A, JP,64-62316,A, and JP,4-309568,A, 20 or less % of the weight of a thing has [the addition of polymerization nature alkyl acid phosphate] antistatic ability inadequate [on the contrary,].

[0006] Then, various devices have so far been taken so that antistatic ability sufficient by using other additives together

with polymerization nature alkyl acid phosphate may be obtained. The Nonion system surfactant is used together in JP,57-65761,A. The phosphoric ester of non-organic functions is used together in JP,1-168771,A. The sulfonic acid is used together in JP,50-109944,A. However, it becomes easy to produce nonuniformity upwards during hardening of a protective coating, and the phosphoric ester of the Nonion system surfactant which is non-functionality, and non-functionality, or addition of a sulfonic acid causes the fall of dedropping antistatic ability from a protective coating by rinsing etc. Moreover, in what added the sulfonic acid, since a sulfonic acid is a hydrophilic property, concomitant use with a low polar compound is difficult, and the degree of freedom of a resin constituent design falls. When the resin constituent was especially applied under the environment of high humidity, this inclination became remarkable, and it was easy to start phase separation between low polar compounds, and there was a problem that a smooth paint film was not obtained. Moreover, when only the surfactant which demonstrates electrification prevention was added, the problem which falls greatly also had a degree of hardness.

[0007] Furthermore, when the above resin constituent was the thing of a comparatively low degree of hardness, it was satisfactory to adhesion with a base material, but when the coat of a high degree of hardness was formed, adhesion with a base material was inadequate. For this reason, the ingredient which has a high degree of hardness, antistatic ability, and adhesion was called for.

[0008]

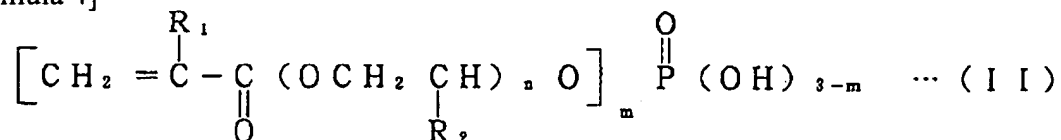
[Problem(s) to be Solved by the Invention] The technical problem which this invention tends to solve has sufficient antistatic ability, a high degree of hardness, good adhesion, and high UV permeability, and a water resisting property is also offering the resin constituent which can offer a good protective coating, and the photo mask which has this protective coating in a list.

[0009]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, the 1st invention of this invention The resin constituent for covering which comes to contain the silane compound expressed with polymerization nature alkyl acid phosphate and the following type (I) as a principal component is offered. The 2nd invention of this invention (A) It consists of an organic compound which has two or more polymerization nature partial saturation double bonds in the silane compound expressed with the polymerization nature alkyl acid phosphate expressed with the following type (II), and the (B) following type (I), and (C) 1 molecule. The resin constituent for covering characterized by coming to blend these at a specific rate and the photo mask which it comes to cover with the hardened material of the resin constituent for these covering as the 3rd invention of this invention are offered.

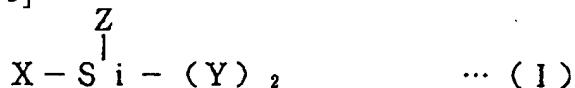
[0010]

[Formula 4]



(上式中、R₁ は水素またはメチル基を、R₂ は水素、メチル基またはハロゲン化メチル基を、mは1または2の整数を、nは1～8の整数を示す。)

[Formula 5]



(上式中、Xはエチレン性不飽和二重結合を有する有機基を、Yはアルコキシ基を、Zはアルコキシ基またはアルキル基を示す。)

[0011] According to the resin constituent for covering of above this inventions, the photo mask with which it has sufficient antistatic ability, a high degree of hardness, good adhesion, and high UV permeability, and a water resisting property also has this protective coating in a good protective coating and a list can be offered easily.

[0012]

[Embodiment of the Invention] Although what denaturalized by glycidyl methacrylate to the copolymer of an acrylic monomer and monofunctional polymerization nature alkyl acid phosphate for the purpose of mainly giving antistatic

ability to the resin constituent for covering of this invention is usable, since the degree of hardness of the coat with which the compound expressed with said formula (II) is obtained is high, polymerization nature alkyl acid phosphate is more desirable. As an example of said formula (II), $\text{CH}_2=\text{CHCOOCH}_2\text{CH}_2\text{OPO}(\text{OH})_2$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{OPO}(\text{OH})_2$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}(\text{CH}_2\text{Cl})\text{OPO}(\text{OH})_2$, $2\text{PO}(\text{OH})$, $2(\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{O})\text{PO}(\text{OH})$, $(\text{CH}_2=\text{CHCOOCH}_2\text{CH}_2\text{O})\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}(\text{OCH}_2\text{CH}_2)_4\text{OPO}(\text{OH})_2$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}(\text{OCH}_2\text{CH}_2)_5\text{OPO}(\text{OH})_2$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}(\text{OCH}_2\text{CH}(\text{CH}_3))_5\text{OPO}(\text{OH})_2$ and $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}(\text{OCH}_2\text{CH}(\text{CH}_3))_6\text{OPO}(\text{OH})_2$ etc. -- it is mentioned, and even if it uses two or more kinds of these, they do not interfere.

[0013] Also in these, it is $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{OPO}(\text{OH})_2$. And $(\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{O})_2\text{PO}(\text{OH})$ is desirable in respect of compatibility and a degree of hardness. In this invention, the blending ratio of coal in the constituent of these polymerization nature alkyl acid phosphate has 21 - 40 desirable % of the weight. At less than 21 % of the weight, it is in the inclination which runs short of the antistatic ability of a protective coating, and if the amount exceeding 40 % of the weight is added, when coloring will break out with hardening and UV permeability will fall, it is in the inclination for a degree of hardness and a water resisting property to fall. Especially a desirable rate is 25 - 35 % of the weight.

[0014] The silane compound used by this invention is expressed with said formula (I), improves adhesion with a base material, improves the waterproof aggravation by adding polymerization nature alkyl acid phosphate to coincidence, and is for making high the degree of hardness of a hardening paint film further. The organic radical and Y in which X in this type (I) has an ethylene nature partial saturation double bond show an alkoxy group, and Z shows an alkoxy group or an alkyl group. Specifically, 3-methacryloxy propyl trimethoxysilane, 3-methacryloxypropyl triethoxysilane, 3-methacryloxy propyl methyl dimethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, a vinyl tris (2-methoxyethoxy) silane, etc. are mentioned. Also in these, 3-methacryloxy propyl trimethoxysilane and 3-methacryloxypropyl triethoxysilane are desirable in respect of adhesion, a water resisting property, and a degree of hardness. The blending ratio of coal in the constituent of this invention of these silanes compound is 3 - 30 % of the weight. When fewer than 3 % of the weight, if the effectiveness of the improvement in adhesion with a base material, waterproof improvement, and the improvement in a degree of hardness is low and the amount exceeding 30 % of the weight is added, a smooth paint film will be difficult to get because of phase separation, and antistatic ability will fall. Especially a desirable rate is 5 - 15 % of the weight.

[0015] In order to obtain a high degree of hardness in the resin constituent for covering of this invention, it is desirable the organic compound which has two or more polymerization nature partial saturation double bonds in 1 molecule, and that molecular weight blends 10,000 or less organic compound more preferably, and the combination of a compound which has three or more polymerization nature partial saturation double bonds in 1 molecule is more desirable. As an example, as a compound which has two polymerization nature partial saturation double bonds in 1 molecule Bisphenol A ethylene oxide denaturation diacrylate, isocyanuric acid ethylene oxide denaturation oxide denaturation diacrylate, Polyethylene-glycol diacrylate and/or methacrylate ("acrylate and/or methacrylate" are called "acrylate (meta)" below.) Polypropylene GURIKORUJI (meta) acrylate, hexamethylene GURIKORUJI (meta) acrylate, Dimethylol tricyclodecane diacrylate, TORIMECHI roll pro pansy (meta) acrylate, pen TAERISURITORUJI (meta) acrylate, GURISERINJI (meta) acrylate, JIPENTAERISURITORUJI (meta) acrylate, etc. are mentioned.

[0016] On the other hand as a compound which has three or more polymerization nature partial saturation double bonds in 1 molecule Trimethylolpropane triacrylate and/or methacrylate, Pen TAERISURITORUTORI (meta) acrylate, GURISERINTORI (meta) acrylate, JIPENTAERISURITORUTORI (meta) acrylate, tris (acryloxyethyl) isocyanurate, and/or tris (methacryloxyethyl) isocyanurate ("acryloxy and/or meta-chestnut ROKISHI" are called "acryloxy (meta)" below.) Pentaerythritol tetrapod (meta) acrylate, dipentaerythritol tetrapod (meta) acrylate, The epoxy group, acrylic acid, and/or methacrylic acid ("an acrylic acid (meta)" is called below.) of dipentaerythritol PENTA (meta) acrylate, dipentaerythritol hexa (meta) acrylate, and an epoxy resin from -- the becoming epoxy (meta) acrylate, the epoxy (meta) acrylate which consists of the poly glycidyl ether and the acrylic acid (meta) of polyhydric alcohol, the urethane acrylate of polyhydric alcohol, etc. are mentioned, and using two or more kinds of these does not interfere, either. Also in these, dipentaerythritol hexa (meta) acrylate or pentaerythritol tetrapod (meta) acrylate is desirable in respect of a degree of hardness.

[0017] In the constituent of this invention, it is desirable to blend the organic compound which has two or more polymerization nature partial saturation double bonds in these 1 molecule 30 to 76% of the weight. At less than 30 % of the weight, the inclination for the degree of hardness of covering to fall is seen, and if the amount exceeding 76 % of the weight is added, the inclination for sufficient antistatic ability and adhesion not to be acquired will be seen. Especially a desirable rate is 35 - 65 % of the weight.

[0018] It is also possible to add many properties of the resin constituent for covering of this invention within limits to

which a reactant diluent, a polymerization initiator, a solvent, a leveling agent, a defoaming agent, or thermal polymerization inhibitor is not remarkably reduced by request to the constituent of this invention which makes an above-mentioned component indispensable, and this invention is not limited to it. A reactant diluent is an organic compound which has one polymerization nature partial saturation double bond in 1 molecule for the purpose of the improvement of spreading nature, and improvement in workability. As an example, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, cyclohexyl (meta) acrylate, benzyl (meta) acrylate, tetrahydrofurfuryl (meta) acrylate, isobornyl (meta) acrylate, 2-(meta) AKURIRO yloxy ethylhexahydrophthalic acid, N-vinyl pyrrolidone, etc. are mentioned.

[0019] A thermal polymerization initiator or a photopolymerization initiator applies the resin constituent of this invention on the surface of a base material, and it adds it in order to carry out bridge formation hardening of this constituent and to make a coat form. As an example of a thermal polymerization initiator, azo compounds, such as peroxides [, such as benzoyl peroxide, G tert-butyl peroxide, dicumyl peroxide and cumene hydroperoxide], azobisisobutyronitril, 2, and 2-azobis (2,4-dimethylvaleronitrile), are mentioned. As an example of a photopolymerization initiator, 2-hydroxy-2-methyl-1-phenyl-1-propanone, 1-(4-isopropyl phenyl)-2-hydroxy-2-methyl-1-propanone, 2-methyl-1-(4-(methylthio) phenyl)-2-morpholino-1-propanone, 1-hydroxy cyclohexyl phenyl ketone, an acetophenone system like benzyl dimethyl ketal, A thioxan ton system like concomitant use of a diketone system like phenyl methoxy diketone, an isopropyl thioxan ton, concomitant use [of p-dimethylamino ethyl benzoate], 2, and 4-diethyl thioxan ton, and p-dimethylamino ethyl benzoate is mentioned. As for these polymerization initiators, 1 - 10 % of the weight is preferably added 0.1 to 20% of the weight to the resin constituent for covering of this invention. Even if it uses together a thermal polymerization initiator and a photopolymerization initiator, they do not interfere. It is also possible to harden with an electron ray in addition to this. In this case, these polymerization initiators are unnecessary.

[0020] The resin constituent for covering of this invention is diluted with a solvent if needed for the improvement of spreading nature, improvement in workability, and thickness adjustment of a protective coating. If the permeability of a protective coating is especially thought as important for exposure-time compaction at the time of photo-mask use, it is desirable to dilute with a solvent and to adjust the thickness of a protective coating thinly. As an example of such a solvent, ester, such as ether, such as ketones, such as aromatic hydrocarbon, such as alcohols, such as ethanol, isopropanol, normal propanol, isobutyl alcohol, and normal butyl alcohol, toluene, and a xylene, an acetone, a methyl ethyl ketone, methyl isobutyl ketone, and a cyclohexanone, and dioxane, ethyl acetate, butyl acetate, ethylcellosolve acetate, and propylene-glycol-monomethyl-ether acetate, is mentioned. However, since there is a possibility of producing the cloudiness from which a solvent becomes a cause depending on the class of base material, it is desirable to use it according to the class of base material, choosing suitably. The resin constituent for covering used by this invention can be easily prepared by mixing an above-mentioned component.

[0021] 0.5-10 micrometers is desirable still more desirable, and 0.7-5 micrometers of thickness of the protective coating formed by this invention are 1-3 micrometers especially preferably. When thickness is thinner than 0.5 micrometers, sufficient antistatic ability and abrasion-proof nature are hard to be obtained, and permeability tends to fall in the thickness exceeding 10 micrometers. The thickness of a protective coating can be changed into arbitration by adjusting the solid content concentration of a resin constituent.

[0022]

[Function] Since the photo mask which has the protective coating and this protective coating which are obtained from the resin constituent for covering of this invention has blended polymerization nature alkyl acid phosphate, it is excellent in the balance of a degree of hardness and antistatic ability compared with the antistatic resin using the conventional surface active agent, and has sufficient antistatic ability which was not obtained in the constituent for which only small quantity uses polymerization nature alkyl acid phosphate. Moreover, the water resisting property which was inadequate when this polymerization nature alkyl acid phosphate was used in large quantities has been improved by considering a specific silane compound as combination, and improvement in a degree of hardness was realized to coincidence. Furthermore, it was compatible in adhesion and a degree of hardness with the base material what added the sulfonic acid was inadequate.

[0023]

[Example] Hereafter, an example and the example of a comparison are given and this invention is explained more concretely. The detail of the used ingredient is as follows.

(Polymerization nature alkyl acid phosphate)

- HOSUMAM : Product made from uni-chemical one, 2-meta-chestnut ROIROKI SHIECHIRU acid phosphate - light ester PA : The product made from Kyoeisha Chemistry, 2-AKURIROIROKISHIE Chill acid phosphate -KAYAMER

PM-2 : [The Nippon Kayaku Co., Ltd. make, 2-meta-KURIRO yloxy] Ethyl acid phosphate - light ester P-1M : [The product made from Kyoeisha Chemistry, 2-meta-KURIRO yloxy] Ethyl acid phosphate - HOSUMA PE : Product made from uni-chemical one, acid phosphoxy Polyoxy-ethylene-glycol mono-meta KURIRO - TO (silane compound) - KBM-503 : the Shin-Etsu Chemical Co., Ltd. make, 3-meta KURIROKISHIPUROPIRUTO RIMETOKI gardenia fruit run -A-174 : The Nippon Unicar make, 3-meta KURIROKISHIPUROPIRUTO RIMETOKI gardenia fruit run - KBM-1003: The Shin-Etsu Chemical Co., Ltd. make, vinyltrimetoxysilane -KBE-503: The Shin-Etsu Chemical Co., Ltd. make, 3-meta KURIROKISHIPUROPIRUTO RIETOKI gardenia fruit run [0024]

(Organic compound which has three or more polymerization nature partial saturation double bonds in 1 molecule) ARONIKKUSU M-450 : - The Toagosei make, pen TAERISURITORUTETO RAAKURI rate - ARONIKKUSU M-305 : [The Toagosei make, pen TAERISURITORUTORI] Acrylate - ARONIKKUSU M-400: Toagosei make JIPENTAERISURITORUPE Mixture of NTA and hexa acrylate (organic compound which has two polymerization nature partial saturation double bonds in 1 molecule)

- ARONIKKUSU M-260 : the Toagosei make, polyethylene GURIKORUJI Acrylate - ARONIKKUSU M-270: The Toagosei make, polypropylene glycol Diacrylate [0025]

(Thermal polymerization initiator)

- Park Mill D : The Nippon Oil & Fats Co., Ltd. make, dicumyl peroxide - NAIPA BMT : The Nippon Oil & Fats Co., Ltd. make, benzoyl peroxide -V-65 : Wako Pure Chem make, 2, and 2-azobis (2, 4-JI methyl valeronitrile)

(Solvent etc.)

- PGMAc : propylene-glycol-monomethyl-ether acetate -MEK : Methyl ethyl ketone -HPA : Hydroxypropyl acrylate (Nonion system surfactant)

- Tween80 : Product made from Kanto Chemistry Polyoxyethylene SORUBITA MMONO oleate (non-organic-functions phosphoric ester compound)

- JAMP-4 : Product made from Johoku Chemistry Butyl acid phosphate [0026] As polymerization nature alkyl acid phosphate, the "HOSUMAM" 25 section, (Example 1) It considers as the organic compound which has three or more polymerization nature partial saturation double bonds in the "KBM-503" 7 section and 1 molecule as a silane compound. The "ARONIKKUSU M-450" 68 section, The "Park Mill D" 5 section was mixed as a thermal polymerization initiator, the ethanol 400 section and the fluorine system leveling agent 1 section were mixed as a solvent, and the resin constituent for covering was prepared. Using a glass substrate with a thickness of 2mm as a base material, the resin constituent for covering was applied by the spin coater so that a protective coating might be set to 2 micrometers, and the protective coating was obtained by holding at 180 degrees C for 15 minutes. In order to investigate the antistatic ability of this protective coating, a degree of hardness, adhesion, a water resisting property, and transparency, a surface-electrical-resistance value, a pencil degree of hardness, grid test, waterproof trial, and evaluation of UV permeability were performed as follows, and the evaluation result was shown in Table 3.

[0027] (Surface-electrical-resistance value) The surface-electrical-resistance value of a protective coating was measured according to JISK6911 under 25**2 degrees C and 65**5% of environment.

(Pencil degree of hardness) The pencil degree of hardness of a protective coating was measured using Mitsubishi Pencil YUNI according to JISK5400.

(Grid test) Evaluation of the adhesion of a protective coating was performed according to the grid test of JISK5400. A judgment is shown by how many pieces had pasted up among the grid of 100 pieces.

(Water resisting property) Observing the appearance after a protective coating is immersed underwater for 1 hour estimated the water resisting property of a protective coating.

(UV permeability) the permeability of the base material with which UV permeability of a protective coating formed the protective coating using UV light (wavelength of 365nm) -- measuring -- a base material -- calculating the reduced property when making independent permeability into 100% estimated.

[0028] (Photoresist patterning) On the glass substrate which formed the chromium thin film layer on the glass substrate, and formed the chromium thin film pattern through resist formation, patterning, etching, and resist exfoliation further, the resin constituent for covering was applied by the spin coater so that a protective coating might be set to 2 micrometers, and the photo mask which has a protective coating was obtained by holding for 15 minutes at 180 degrees C. To copper clad laminate, it is the negative-mold photoresist PERM. N-HC40 (Toagosei make) was applied using the bar coating machine, desiccation was performed for 5 minutes at 90 degrees C, and the resist film of 13 micrometers of thickness was obtained. Next, using photoresist double-sided baking opportunity HTE-106S (Product made from High-tech), vacuum adhesion of said photo mask was carried out on said resist film, and it exposed with the 5kW ultrahigh pressure mercury lamp. Light exposure is 200 mJ/cm². It carried out and the exposure part was stiffened. Thus, dissolution removal of the unexposed part was carried out for the obtained resist film in the sodium-

carbonate water solution of 1% of concentration using the conveyor type spray developing machine (made in a KIMURA Inc. etching lab). Observing the appearance of the used photo mask and the appearance of the resist film in which the pattern was formed estimated.

[0029] (Examples 2-7) Using what was indicated to Table 1 as a component of polymerization nature alkyl acid phosphate, a silane compound, the organic compound that has two or more polymerization nature partial saturation double bonds in 1 molecule, and others, it mixed and the resin constituent for covering was prepared. Next, this constituent was applied on the substrate like the example 1, and the protective coating was obtained. The same evaluation as an example 1 was performed to this protective coating, and patterning of a photoresist was performed using the photo mask which comes to cover this protective coating further. The evaluation result was shown in Table 3.

[0030] As polymerization nature alkyl acid phosphate, the "HOSUMAM" 10 section, (Example 1 of a comparison) It considers as the organic compound which has three or more polymerization nature partial saturation double bonds in the "A-174" 25 section and 1 molecule as a silane compound. The "ARONIKKUSU M-450" 65 section, The "Park Mill D" 5 section was mixed as a thermal polymerization initiator, the methyl-ethyl-ketone 400 section and the fluorine system leveling agent 1 section were mixed as a solvent, and the resin constituent for covering was prepared. Next, except having used this constituent, it applied on the substrate like the example 1, and the protective coating was obtained. In order to investigate the antistatic ability of this protective coating, a degree of hardness, adhesion, a water resisting property, and transparency, a surface-electrical-resistance value, a pencil degree of hardness, grid test, waterproof trial, and evaluation of UV transmission were performed, and patterning of a photoresist was performed using the photo mask which comes to cover this protective coating further. The evaluation result was shown in Table 3.

[0031] (Examples 2-7 of a comparison) Using what was indicated to Table 2 as a component of polymerization nature alkyl acid phosphate, a silane compound, the organic compound that has two or more polymerization nature partial saturation double bonds in 1 molecule, and others, it mixed and the resin constituent for covering was prepared. Next, this constituent was applied on the substrate like the example 1, and the protective coating was obtained. The same evaluation as an example 1 was performed to this protective coating, and patterning of a photoresist was performed using the photo mask which comes to cover this protective coating further. The result was shown for the evaluation result in Table 3.

[0032]

[Table 1]

表 1 実施例の組成

	重合性酸性リ ン酸エステル		シラン化合物		重合性不飽和二 重結合を 3 個以 上 (2 個) 有す る有機化合物		その他	
	種類	部	種類	部	種類	部	種類	部
実施例 1	ホスマー M	25	KBM-503	7	アロニック SM-450	68	パークミルD レベリング剤 エタノール	5 1 400
実施例 2	ライトエ ステルPA	22	A-174	20	アロニック SM-305	45	HPA ナイパー-BMT レベリング剤 エタノール	13 5 1 400
実施例 3	KAYAMER PM-2	30	KBM-100	20	アロニック SM-400	50	パークミルD レベリング剤 MEK	5 0.5 400
実施例 4	ライトエ ステル P-1 M	30	A-174	10	アロニック SM-450	60	V-65 レベリング剤 PGMAc	5 1 400
実施例 5	ホスマー PB	35	KBE-503	20	アロニック SM-400	45	ナイパー-BMT レベリング剤 MEK	5 0.5 400
実施例 6	KAYAMER PM-2	35	A-174	8	アロニック SM-400 (アロニック クスM-260)	45 12	ナイパー-BMT レベリング剤 MEK	5 0.5 400
実施例 7	ライトエ ステル P-1 M	22	A-174	15	アロニック M-400 アロニック M-305	30 33	パークミルD レベリング剤 PGMAc	5 1 400

[0033]

[Table 2]

表2 比較例の組成

	重合性酸性リン酸エステル		シラン化合物		重合性不飽和二重結合を3個以上(2個)有する有機化合物		その他	
	種類	部	種類	部	種類	部	種類	部
比較例1	ホスマー M	10	A-174	25	アロニック スM-450	65	パークミルD レベリング剤 MEK	5 1 400
比較例2	ホスマー M	50	A-174	10	アロニック スM-450	40	パークミルD レベリング剤 MEK	5 1 400
比較例3	ホスマー M	30	-	-	アロニック スM-450	70	パークミルD レベリング剤 MEK	5 1 400
比較例4	KAYAMER PM-2	25	A-174	40	アロニック スM-450	35	パークミルD レベリング剤 MEK	5 1 400
比較例5	ホスマー M	30	A-174	20	アロニック スM-450 (アロニック クスM-270)	15 35	パークミルD レベリング剤 MEK	5 1 400
比較例6	KAYAMER PM-2	15	A-174	10	アロニック スM-450	60	Tween80 パークミルD レベリング剤 MEK	15 5 1 400
比較例7	-	-	A-174	20	アロニック スM-450	50	JAMP-4 パークミルD レベリング剤 MEK	30 5 1 400

[0034]

[Table 3]

表3 実施例および比較例の評価結果

	外観	表面抵抗 値 (Ω)	鉛筆 硬度	ガッ 目 テスト	耐水性	UV透過 率(%)	フォトマスク 外観	レジスト 外観
実施例1	良好	2×10^{12}	5H	100/100	変化なし	92	変化なし	良好
実施例2	良好	5×10^{11}	5H	100/100	変化なし	92	変化なし	良好
実施例3	良好	4×10^{12}	5H	100/100	変化なし	91	変化なし	良好
実施例4	良好	6×10^{11}	5H	100/100	変化なし	91	変化なし	良好
実施例5	良好	8×10^{11}	4H	100/100	変化なし	90	変化なし	良好
実施例6	良好	2×10^{12}	5H	100/100	変化なし	91	変化なし	良好
実施例7	良好	1×10^{12}	5H	100/100	変化なし	93	変化なし	良好
比較例1	良好	2×10^{13}	5H	100/100	変化なし	94	変化なし	良好
比較例2	黄色に着色	5×10^9	<2H	100/100	変化なし	84	傷あり	良好
比較例3	良好	1×10^{13}	2H	0/100	剥離	91	変化なし	良好
比較例4	凹凸が激しい							
比較例5	良好	6×10^{12}	<2H	100/100	変化なし	94	傷あり	良好
比較例6	良好	6×10^{12}	3H	20/100	変化なし	91	変化なし	良好
比較例7	凹凸が激しい							

[0035]

[Effect of the Invention] According to this invention, it became possible to obtain the photo mask which has the protective coating to which it is satisfied with the conventional resin constituent of sufficient antistatic ability which was not able to be attained, a high degree of hardness, good adhesion, and high UV permeability, and a water resisting property also becomes a good resin constituent for covering, and a list from this constituent.

[Translation done.]

* NOTICES *

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

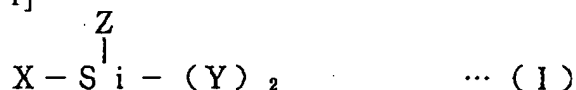
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The resin constituent for covering which consists of a silane compound expressed with polymerization nature alkyl acid phosphate and the following type (I), and is characterized by the content of said silane compound being 3 - 30 % of the weight.

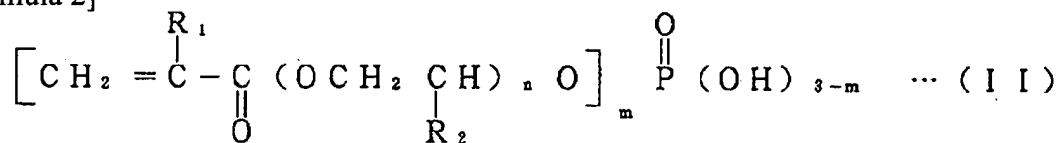
[Formula 1]



(上式中、Xはエチレン性不飽和二重結合を有する有機基を、Yはアルコキシ基を、Zはアルコキシ基またはアルキル基を示す。)

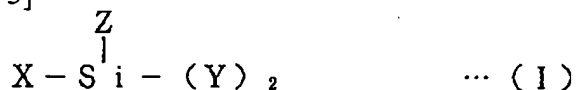
[Claim 2] (A) For 30 % of the weight and the 3 - (C) component, 21 - 40-% of the weight and (B) component is [each blending ratio of coal] the resin constituent for covering with which it is characterized by consisting of an organic compound which has two or more polymerization nature partial saturation double bonds in the silane compound expressed with the polymerization nature alkyl acid phosphate expressed with the following type (II), and the (B) following type (I), and (C) 1 molecule, and the (A) component being 30 - 76 % of the weight.

[Formula 2]



(上式中、R₁は水素またはメチル基を、R₂は水素、メチル基またはハロゲン化メチル基を、mは1または2の整数を、nは1～8の整数を示す。)

[Formula 3]



(上式中、Xはエチレン性不飽和二重結合を有する有機基を、Yはアルコキシ基を、Zはアルコキシ基またはアルキル基を示す。)

[Claim 3] The photo mask which it comes to cover with the hardened material of the resin constituent for covering according to claim 1 or 2.

[Translation done.]